BULK NANOSTRUCTURED REFRACTORY METALS WITH ENHANCED MECHANICAL PROPERTIES PRODUCED BY EQUAL CHANNEL ANGULAR PRESSING

Final Technical Report

by
R.Z. Valiev and I.V. Alexandrov
(11 June 2003 - 10 November 2003)

United States Army

EUROPEN RESEARCH OFFICE OF THE U.S. ARMY

London England

CONTRACT NUMBER: N62558-02M-6024

Name of Contractor **Institute of Physics of Advanced Materials**
Ufa State Aviation Technical University

Approved for Public Release; Distribution unlimited

FINAL REPORT

A. The Cover Page

(1) Bulk nanostructured refractory metals with enhanced mechanical properties produced by equal channel angular pressing
(2) Professor R.Z. Valiev
(3) Professor V.S. Zhernakov
(4) N62558-02M-6024
(5) Final Report
(6) 11 June 2003 - 10 November 2003
(7) The Research reported in this document has been made possible through the support and sponsorship of the U.S. Army. This report is intended only for the internal management use of the Contractor and U.S. Government.

REPORT DOCUMENT PAGE			*Form Approved* *OMB No 0704*
1. AGENCY USE ONLY.	**2. REPORT DATE** March 10, 2003	**3. REPORT TYPE AND DATES** Final Report (11.06.2003 –10.11.2002)	
4. TITLE AND SUBTITLE Bulk nanostructured refractory metals with enhanced mechanical properties produced by equal channel angular pressing			**5. FUNDING NUMBERS** N62558-02M-6024
6. AUTHORS: Prof. R.Z. Valiev, Prof. I.V. Alexandrov			
7. PERFOMING ORGANIZATION NAMES AND ADDRESS Institute of Physics of Advanced Materials, Ufa State Aviation Technical University. 12 K. Marx St., Ufa 450000, Russia			**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING / MONITORING AGENCY NAME AND ADDRESS U.S. Government and European Research Office of the U.S. Army. USARDSG-UK, FISCAL-OFFICE, EDISON HOUSE, 223 OLD MARYLEBONE ROAD, LONDON NW1 5TH, UNITED KINGDOM			**10. SPONSORING / MONITORING AGENCY REPORT NUMBER**
11. SUPPLEMENTARY NOTES In co-operation with Dr. R. Dowding, U.S. Army Research Laboratory Aberdeen Proving Ground, Maryland 21005-5066			
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release, distribution unlimited			**12b. DISTRIBUTION CODE**

13. ABSTRACT

The main aim of the current project has been to produce a batch of bulk billets with ultrafine-grained (UFG) microstructure and enhanced strength made of two refractory metals such as tungsten and tantalum. To process bulk W billets with UFG structure having a long-length size more than 100 mm we have developed and successfully used a new approach based on a combination of equal angular pressing (ECAP) and further extrusion. In frames of this project we could also fabricate UFG Ta with strength increased more than 3 times.

14. SUBJECT TERMS Severe plastic deformation, ultrafine-grained structure, W and Ta, equal-channel angular pressing, refractory materials, strength and ductility			**15. NUMBER OF PAGES**
			16. PRICE CODE
17. SECURITY CLASSIFACATION OF REPORT Unclassified	**18. SECURITY CLASSIFICATION OF THIS PAGE** Unclassified	**19. SECURITY CLASSIFICATION OF ABSTRACT** Unclassified	**20. LIMITATION OF ABSTRACT** UL

Abstract

The main aim of the current project has been to produce a batch of bulk billets with ultrafine-grained (UFG) microstructure and enhanced strength made of two refractory metals such as tungsten and tantalum. To process bulk W billets with UFG structure having a long-length size more than 100 mm we have developed and successfully used a new approach based on a combination of equal angular pressing (ECAP) and further extrusion. In frames of this project we could also fabricate UFG Ta with strength increased more than 3 times.

Keywords: severe plastic deformation, ultrafine-grained structure, W and Ta, equal-channel angular pressing, refractory materials, strength and ductility

1. INTRODUCTION

For the recent decade it has been well demonstrated that a formation of nanostructures in crystalline materials can lead to their new and often unique properties [1-4]. Regarding mechanical properties, a special interest has been paid to achieving high strength and high ductility, superplasticity at low temperatures or/and high strain rates, enhanced fatigue properties and toughness. In this connection the development of severe plastic deformation (SPD) techniques seems to be very perspective. These techniques allow refining microstructure in bulk metal and alloy billets up to submicro- and nanocrystalline sizes. This approach, put forward at our lab about 10 years ago [5], has been recently developed and widely used. It has been applied not only for pure metals, but also for many commercial alloys [3, 6-7].

However the application of ECAP to hard-to-deform materials leads usually to fast destruction of billets due to their low workability.

Within the frames of our previous projects EARO #68171-99-M-6634 and #68171-01-M-5641 we managed for the first time to refine microstructure in such hard-to-deform and low-ductile materials as CP W and its alloys by ECAP. We showed, that the use of 2-3 passes of ECAP leads to a substructure formation with subgrain sizes (fragments) less than 1-2 μm. This substructure is transforming subsequently into ultrafine grains having a size of about 0.5 μm with an increase in the number of passes during optimal ECAP regimes.

Recently in work [8] there has been made the first demonstration of a possibility to refine microstructure in Ta by means of ECAP. As a result of this treatment with a few

passes in combination with recrystallization annealing in Ta there was obtained a subgrain microstructure with the size of subgrains equal to 100-350 nm and having mostly low angle boundaries. However, in order to achieve simultaneously enhanced strength and enhanced ductility in SPD produced materials, as we know presently, it is important to form an UFG structure with high-angle grain boundaries. It becomes possible by means of larger severe deformation, typically with true strains higher than 6 [3,10].

The investigations conducted in [9] show, that additional microstructure refining, and, as a consequence, enhancing of mechanical properties of metals and alloys is possible as a result of an application of complex treatment, based on a combination of ECAP and conventional deformation methods, such as rolling or extrusion. This approach appears especially topical when treating low-ductile and hard-to-deform materials. Besides, with an application of complex deformation treatment it makes possible to process bulk UFG billets having different geometry with a high level of strength properties.

The main aim of the current project has been to obtain a batch of long-length UFG W bulk billets 100 mm long and 10 mm in diameter with enhanced strength. For this purpose we applied a special approach, based on a combination of ECAP and extrusion. The second task of the project was an investigation of ECAP of Ta aimed at processing of UFG structure.

2. MATERIAL AND EXPERIMENTAL PROCEDURES

Experimental investigation of the method for processing of longer sized UFG W billets was performed on commercially available tungsten manufactured in Russia by powder metallurgy methods. The material represented rods with a diameter of 15 mm. Processing peculiarities and a chemical composition of investigated W are represented in detail in the project report. Development and application of the processing approach was performed on W, delivered by the Customer in a form of a rod 16 mm in diameter and 600 mm long.

Pure tantalum was delivered for investigations as a rod 17.5 mm in diameter and 300 mm long.

To realize ECAP processes and extrusion the press-forging equipment – hydropress DB2426 with up to160 tons by force with the velocity of traverse moving equal to 6 mm/s was used.

To demonstrate an ultimate microstructural refining in Ta by SPD high pressure torsion (HPT) straining was also performed using Bridgman anvils under an imposed pressure of about 6 GPa on electropolished specimens in a shape of a disc 10 mm in diameter and 0.5 mm thick.

Microstructure investigations of the SPD-processed billets were performed in transverse and longitudinal section using optical microscopy (OM) (NEOPHOT-32), scanning and transmission electron microscopy (SEM and TEM) (JEM-100). For the OM, chemical etching of polished metallographic specimens in a 3% solution of hydrogen peroxide was carried out to prepare the specimens. TEM foils of pure W were prepared by jet-polished in a water solution of sodium hydroxide at 10 °C and 10 V and a solution of CH_3OH (94%), H_2SO_4 (5%) and HF (2%) at -40 °C was used to prepare foils of Ta. The mean grain size and the volume fraction of ultra-fine grains were determined by the linear intercept method.

Mechanical properties were determined by the results of the microhardness measurements and tensile tests. Microhardness measurements were made by the Vickers method in transverse and longitudinal sections of the metallographically polished samples under a load of 200 g applied for 15 s. The data point represents the average of 10 measurements. Tensile specimens having gauge dimensions 3x2x15 mm^3 were cut by spark erosion from pressing billets in longitudinal directions. Tensile tests were conducted at room temperature, and at initial constant strain rate $5x10^{-4}$ s^{-1} using screw-driven Instron machine. The yield stress was determined as $\sigma_y=P/S_o$ - stress, at which the residual elongation reaches 0.2%. Ultimate tensile strength was determined as a ratio of the maximal load to the initial square of the traverse section of the working part of samples $\sigma_u=Pmax/S_o$. Failure stress corresponds to the ratio of P effort at the moment of the sample's destruction to the minimal square of the working parts of the destroyed sample σ_f.

3. SPD PROCESSING

3.1. Processing of longer sized UFG W billets

To implement the project task, aimed at producing of relatively long bulk nanostructured billets of pure W 10 mm in diameter and 100 mm long with a grain size

less than 0.5 μm having enhanced mechanical properties, we developed a complex processing approach, which includes the following:

- Processing of rods ∅16 mm×60 mm having ultrafine-grained (UFG) structure by ECAP.
- Processing of rods ∅10 mm×100 mm by means of direct pressing (extrusion) of ECAP billets.
- Investigations of microstructure and mechanical properties of billets in the initial state, after ECAP and its subsequent direct pressing.

At the first stage a modification of ECAP die-set was made in order to form UFG structure. At the second stage the extrusion of ECAP billets was conducted in order to obtain billets having a required size and additional strengthening. A scheme for UFG billets processing is shown in Fig. 1. A necessity to combine ECAP with a subsequent extrusion is connected first of all with the technical task concerning the processing of billets having the ratio L/d=10, which is essentially higher than typical ECAP billets having the ratio L/d=5-6. An enhanced length of the ECAP billet leads to additional problems connected with an increase in endurance of the die-set.

The validity of the given approach, based on a combination of ECAP and additional rolling or extrusion, was shown in our recent papers on commercially pure Ti. In the case of CP Ti the use of the complex treatment allowed producing the UFG structure with a mean grain size of 0.2 μm and increasing the ultimate tensile strength almost 2.5 times from 450 MPa to 1100 MPa [9].

To realize the given approach the die-sets for ECAP of W in isothermic conditions and further extrusion were developed and used (Fig. 2).

First experimental investigations were conducted on CP W billets manufactured in Russia by powder metallurgy methods. In more detail the processing by ECAP of W was developed and reported when fulfilling our previous project N68171-01-M-5641. Taking into account these results UFG billets were processed by ECAP on the route C at a heating temperature of 1100-1200 °C, with an angle of the die-set channels' intersection of 120°. The size of the initial billets of CP W was ∅16x80 mm. After ECAP and mechanical treatment it became ∅15x60 mm. Mechanical treatment was carried out in order to remove the material, which was not well worked through at the end parts of the billets.

Extrusion of UFG billets after ECAP was performed at the heating temperature of the billet 1000 ºC and a pressing rate of 6 mm/sec using another die-set for extrusion. The extrusion of W billets was carried out by two cycles (Fig. 3 a, b). The strain per one

cycle made up 25%. As a result of two cycles of extrusion, a billet 11 mm in diameter and 134 mm long was obtained. Here the elongation ratio made up more than 2, and the accumulated strain was e=0,6.

Thus it has been shown on the example of W fabricated by the powder metallurgy method that the proposed approach has good prospects for producing of long-sized W billets.

However, W billets delivered by the Customer get destroyed already after 1-2 ECAP passes at 1050 °C. An increase in temperature up to 1100-1200 °C has not also led to a successful ECAP with several passes (Fig. 4). Obviously, low deformability of this W during ECAP can be originated with the content and character of impurities' distribution, as well as the prehistory of the material processing. Only the use of stronger protecting shell made it possible to process integral W samples after 8 passes of ECAP. Considering low deformability of the given W, subsequent extrusion was conducted also at a temperature higher than 1000 °C.

3.2. Development of SPD processing of Ta

Tantalum (Ta) has been the other subject for investigation in the current project. It is known [3,10] that in order to achieve simultaneously enhanced strength and ductility in SPD produced materials it is important to form an UFG structure with high-angle grain boundaries. It becomes possible by means of larger severe deformation, typically with true strains higher than 6. Recent investigations have demonstrated the ability to produce such homogeneous nanostructures with a grain size of about 100 nm and less by means of high pressure torsion (HPT). This method may be considered as one of techniques for bulk nanostructred materials processing [3].

In this research HPT straining was performed on commercially available Ta manufactured by powder metallurgy methods with an average subgrain size of about 5 μm. The specimens having a form of a disk 10 mm in diameter and 0.4 mm thick were treated at room temperature by 5 turns under the imposed pressure of about 6 GPa. The logarithmic true strain was e=6. HPT straining of Ta at room temperature has shown a possibility to process samples without microcracks. The microhardness after HPT strain was almost 4 times as large as the microhardness in the as-received state. Investigations of structural macrohomogeneity by measurements of microhardness radial distribution have shown that the microhardness in the center of HPT samples is

lower than in the periphery and it is equal to 1.7 GPa. This is connected with some difference in accumulated strains in the center and periphery of the samples.

A possibility to process Ta at room temperature by HPT allowed us starting the research, aimed at microstructure refining and enhancing of mechanical properties of bulk Ta billets by means of ECAP.

ECAP was carried out at room temperature using the die-set with an angle of the channels' intersection equal to 90°. Shear strain for each pass in the area of the channels' intersection was equal approximately to 1 for an angle of 90° [3]. To process Ta billets without failure a special die-set with backpressure was applied. The experiments on ECAP of Ta were carried out on route Bc (turn of the billet 90° clockwise along the longitudinal axis of the billet). This route usually makes it possible for us to obtain the equiaxed structure [3] more effectively. As a result of 6 cycles of ECAP an integral billet was processed (Fig. 5, a). At that the accumulated strain consisted $e \approx 6$. A further increase in the number of cycles of ECAP up to 8 allowed also preserving the integrity of the billet (Fig. 5, b).

4. MICROSTRUCTURE REFINEMENT AND STRENGTH

4.1 Commercially pure tungsten

As it was mentioned above the goal of the combined treatment by ECAP + extrusion is not only the processing of billets of the required geometry but also enhancing of strength properties as compared to ECAP at a cost of additional microstructure refining as a result of a subsequent extrusion. Meanwhile, it is well known that the deformation by means of extrusion may contribute to a development of a non-equiaxed grain shape and as a consequence to anisotropy of mechanical properties [11]. In this connection the aim of the current structural investigations was to study microstructure changes as a result of extrusion of UFG W, processed by ECAP. A detailed investigation of W UFG structure formation depending on ECAP regimes was represented in the final report on our previous project N 68171-01-M-5641.

The investigations were conducted on the billets of commercially available W manufactured in Russia. As a result of ECAP in a temperature range of 1100-1200 °C with an angle of channels' intersection equal to 120° in W, possessing initially elongated grains with a diameter of 60-80 μm and an aspect ratio of about 10, the UFG structure

is being formed after 8 cycles. The average grain size of the structure is less than 1 μm (Fig. 6 a, b). Meanwhile, the degree of the grains' elongation in the longitudinal section of the billet has decreased from 10 to 2.2 after ECAP. The results of TEM investigations of the billets after two cycles of extrusion are represented in Fig. 6, c, d. The inspection performed testifies to some additional refinement of the microstructure up to 0.5-0.7 μm. Investigations of the longitudinal section of the deformed billet showed, that as a result of extrusion with the mentioned regimes the aspect ratio of grains increased from 2.2. to 2.9.

The results of microhardness measurements showed, that Hv value increased from 4.5 GPa in the initial state to 5.6 GPa after ECAP. The result of additional extrusion is an increase in the microhardness value up to 6.1 GPa. Microhardness measurements in two perpendicular sections of the billet revealed also a decrease in the anisotropy of strength properties of W alongside with an increase in the accumulated strain. The achieved enhancing of the microhardness value as a result of a complex treatment by ECAP and extrusion of W billets is new phenomenon. As it was mentioned in [12] higher hardness could be obtained during ECAP of W, but only by decreasing of the processing temperature. However, the processing by ECAP and extrusion enables to produce W UFG billets having also the necessary geometry.

Thus, the results of the conducted investigations showed that by the combination of ECAP and extrusion we could fabricate UFG W billets up 11 mm in diameter and 130 mm long and also refine additionally the microstructure and enhance the strength.

Using similar regimes we have produced a batch of W billets out of the material supplied by the Customer, which are to be delivered to the Customer.

4.2. UFG Ta processed by HPT and ECAP

TEM and SAED examinations have shown that HPT leads to a strong microstructural refinement especially at the periphery of HPT samples (Fig. 7). Grains were slightly elongated and their sizes were 200 nm long and 100 nm wide (measured from the dark field image).

The SAED pattern contains numerous diffraction spots randomly arranged in rings. This indicates that grain boundaries are mainly of high-angle misorientations. A local distortion of the electron microcopy contrast in the bright field image indicates the presence of high internal stress due to high-density dislocations in vicinity of boundaries. The microstructure of center part of the HPT- processed Ta is different from

the periphery part. Here a banded substructure about 1 μm long and 200-500 nm wide was formed.

Investigations conducted testify to the fact that the UFG structure formation in Ta with a mean grain size less than 0.5 μm is possible as a result of severe plastic deformation. One may suppose that such a refinement of microstructure can be achieved by means of ECAP with larger straining (amount of passes should be higher than 6).

Structural investigations showed, that as a result of ECAP with the number of cycles equal to 8 the UFG structure is being formed in Ta. As can be seen in Fig. 8, after such processing there occurs a formation of a rather ultrafine-grained structure, equiaxed and sufficiently homogeneous both in the transverse and the longitudinal sections of a billet. The mean grain size of this pressing state cannot be estimated by OM observation.

Microhardness investigations showed that testing materials are appreciably strengthened after ECAP. After 8 passes values of microhardness achieved 2483 MPa as compared to 1040 MPa in the initial state, but it is still a bit less than after HPT.

Mechanical tensile tests at room temperature showed, that as a result of ECAP with a number of cycles equal to 8 the ultimate tensile strength of Ta has increased more than 3 times (Table 1). At the same time the total elongation has decreased up to 10% due to a sharp decrease in the uniform elongation. The data represented in the Table show that the values σ_y and σ_u as a result of ECAP are increasing and become similar due to a quicker growth of σ_y. If before ECAP $\sigma_y / \sigma_u = 0.67$, then after $\sigma_y / \sigma_u = 0.78$. The ratio σ_y / σ_u is an important characteristics of the mechanical behavior of the material, which shows the resource of the deformation stability or disposition of the material to localization of deformation. At $\sigma_y / \sigma_u = 1$ there will be achieved a marginal state (when the plastic deformation is non-stable from the start due to a low capability of the material to strain hardening). The obtained results testify, that ECAP of Ta with a number of cycles equal to 8, is not a marginal state and its further hardening by means of enhancing the level of the accumulated strain is possible.

Table 1. Mechanical properties of Ta in the as-received state and after ECAP (8 cycles)

State	*Yield stress, σ_y MPa*	*Ultimate tensile strength, σ_u MPa*	*Fracture stress, σ_f MPa*	*Elongation, %*	*Reduction, %*
As received	139	206	529	50	80
ECAP-8 passes	533	680	910	10	59
Ratio of mechanical properties after and before ECAP	3.8	3.3	1.7	0.2	0.74

5. SUMMARY

Investigations, which had been started in our previous annual ERO project #68171-01-M-5641, revealed a possibility of strong grain refinement in W using equal-channel angular pressing, In the frames of the current project we have conducted investigations aimed at obtaining of a batch of long-sized UFG W bulk billets larger than 100 mm in length and 10 mm in diameter applying a combination of ECAP and extrusion. It has been shown that such a combination allows not only producing billets of a necessary size, but also further enhancing their strength. The latter is evidently associated with greater microstructure refinement by additional extrusion as compared to ECAP.

The second task of the current project was the investigation of Ta processing by ECAP aimed at producing UFG structure. The conducted investigations testify to the fact that the UFG structure formation in Ta with a mean grain size less than 0.5 μm is possible as a result of severe plastic deformation. The ECAP with the route Bc allows obtaining of integral bulk UFG Ta billets. As a result of such grain refining the tensile strength of Ta has increased more than 3 times preserving sufficient ductility.

These investigations demonstrate extraordinary properties in UFG W and Ta, in particular achieving of high-strength and ductility at room temperature that may be a new step for their application.

6. REFERENCES

1. Gleiter H., Nanostructured Materials: Basic Concepts and Microstructure, Acta materialia, Vol. 48, 2000, pp. 1-29.
2. Morris D.J.. In: Mechanical Behavior of Nanostructured Materials. Switzerland: Trans Techn. Publ., 1998, pp. 85-.
3. Valiev R.Z., Islamgaliev R.K., Alexandrov I.V., "Bulk Nanostructured Materials from Severe Plastic Deformation", Prog. Mater. Sci., Vol. 45, 2000, pp. 103-189.
4. McFadden S.X., Mishra R.S., Valiev R.Z., Zhilyaev A.P., Mukherjee A.K., Low-Temperature Superplasticity in Nanostructured Nickel and Metal Alloys, Nature, v. 398, 22 April 1999, pp. 684-686.
5. Valiev R.Z., Korznikov A.V., and R.R. Mulyukov, "Structure and Properties of Ultrafine-Grained Materials", Mater. Sci. Eng., A168, 1993, pp. 141-148.
6. Proceedings of the NATO ARW on Investigations and Applications of Severe Plastic Deformation, NATO Sci. Series, eds. Lowe, T.C. and Valiev, R.Z. Kluwer Publ., 80, 2000.
7. Stolyarov V.V. and R.Z. Valiev. Effect of Heating and Aging in Bulk Metastable Nanostructured Alloys. Ultrafine Grained Materials, TMS, 2000, pp. 351-360.
8. Hartwig K.T., Mathaudhu S.N., Maier H.J. and I. Karaman, Hardness and Microstructure Changes in Severely Deformed and Recrystallized Tantalum. Ultrafine Grained Materials II, TMS, 2002, pp. 151-160.
9. Stolyarov V.V., Zhu Yu.T., Alexandrov I.V., Lowe T.C. and R.Z. Valiev, Grain refinement and properties of pure Ti processed by warm ECAP and cold rolling, Mater. Science and Eng A343, 2003, pp. 43-50.
10. Valiev R.Z., Alexandrov I.V., Zhu Yu.T., Lowe T.C., Paradox of strength and ductility in metals processed by severe plastic deformation, J. Mater res., V. 17, No. 1, Jan. 2002, pp. 5-8.
11. Trefilov V.I., Milman Yu.V. and S.A. Firstov, Physical Bases of Strength of Refractory Metals, ‘Naukova Dumka’ Publ., Kiev, 1975, 315 p. (in Russian).
12. Alexandrov I.V., Raab G.I., Kazyhanov V.U., Shestakova L.O., Valiev R.Z., Dowding R.J., Ultrafine-grained tungsten produced by SPD techniques, Ultrafine Grained Materials II, TMS (The Minerals, Metals and Materials Society), 2002, pp. 199-207.

7. APPENDIX (SEE THE PDF FILE ATTACHED)